Preface

Phenomena due to chemical bond reformation and relaxation are ubiquitous and important. A consistent and systematic understanding of such matters is yet urgently needed, which is the driving force behind the author's efforts in the past two decades.

Pauling indicated in 1939 that the nature of the chemical bond bridges the structures and properties of crystals and molecules. In order to change the physical properties of a substance, one has to control the processes of formation, dissociation, relaxation, and vibration of the chemical bond. The foremost task for accomplishing such goals is to correlate the detectable properties of a material to the parameters of all bonds and nonbonds involved, and to ascertain the interdependence of various properties. Consistent insight into the nature, length, and the energy of the chemical bonds and the associated energetics and dynamics of densification, localization, polarization, and redistribution of electrons during the process of bond reformation and relaxation are essential. Hence, identifying and subsequently controlling the factors and efficient means in engineering bonds and electrons are the ultimate objectives of the community of condensed matter physics and chemistry. The aim of this book is to explore these perspectives.

This book is composed of four parts:

Part I deals with the formation and relaxation dynamics of bonds and nonbonds during chemisorption of O, N, and C to the skins of solid specimens from the perspectives of chemical bond, energy band, surface potential barrier (3B), and their correlation. This part demonstrates that: (i) sp^3-orbit hybridization is necessary for O, N, and C interacting with atoms in the solid phase to form H_2O, NH_3, and CH_4-like tetrahedral structures, which determines the crystallography, morphology, potential barrier, band structure, and the chemical physical properties of the chemisorbed skins; (ii) chemisorption modifies the valence band of the host with four additional energy states, i.e., bonding electron pairs, nonbonding lone pairs, antibonding dipoles, and electronic holes. Such a practice formulates the valance evolution dynamics of atoms on oriented and reconstructed surfaces in different phases of Ag, Cu, Co, Ni, V, Pd, Pt, Ru, diamond, and N and C reacting with Ni surfaces as well; (iii) numerical analysis of measurements results in the quantification of the Cu_3O_2 bond geometry and its four-stage formation and relaxation dynamics as well as the N–Ni and C–Ni bonding dynamics and bond stress; (iv) the 3B premise unifies and empowers the experimental techniques for crystal geometry (LEED, XRD), surface morphology (STM), electron binding energy (STS, UPS, XPS), lattice vibration frequency (Raman, EELS), and thermal desorption (TDS) in terms of bonding and electronic dynamics. It is emphasized that the concept of solid skin up to three atomic layers thick describes better the properties and processes at the solid/vacuum interface than the conventional concept of surface without invoking thickness.

Part II is focused on the relaxation of bonds between atoms with fewer neighbors than the ideal in bulk with unraveling of the bond order-length-strength (BOLS) correlation, which clarifies the difference in nature between nanostructures and bulk of the same substance. This part proves that: (i) bonds between undercoordinated atoms become shorter and stronger; (ii) bond contraction increases the local density of bonding electrons and binding energy while bond strengthening deepens the interatomic potential wells and results in quantum entrapment; (iii) the densely and locally entrapped bonding electrons in turn polarize the weakly bound nonbonding electrons (NEP) to form Dirac-Fermi polarons with emergence of properties that bulk parents do not demonstrate; (iv) interaction between undercoordinated atoms in the skin and the fraction of such undercoordinated atoms determine the unusual behavior of nanostructures. The BOLS correlation clarifies the common origin for the unusual performance of defects, surfaces, grain boundaries, and nanostructures of various shapes in chemistry, dielectrics, electronics, magnetism, mechanics, thermodynamics, phononics, and photonics. Based on the core–shell configuration and the local bond average (LBA) approach, the BOLS-NEP notation reconciles the size and shape dependence of known bulk properties and the emerging anomalies of materials at the nanoscale such as catalytic, magnetic, conductor–insulator transition, topologic insulation, etc. The new degree-of-freedom of crystal size results in determination of the energy levels of an isolated atom, the specific heat per bond, etc. It is emphasized that the size-induced emergence of properties are equally important to the size-induced change of known bulk properties at the nanoscale.

Part III deals with the relaxation dynamics of bonds under heating and compressing and describes the rules governing the temperature- and pressure-resolved elastic and plastic properties of under- and hetero-coordinated systems. This part shows that: (i) binding energy density determines the elasticity and the yield strength; the atomic cohesive energy determines the thermal stability of materials; and the applied forces in measurements create defects and heat the specimen; (ii) undercoordination-induced energetics determines the unusual mechanical performance of atomic chains, atomic sheets, nanotubes, nanowires, point defects, nanograins, liquid and solid skins, and hetero-junction interfaces; (iii) the enhancement of elasticity and polarization of the skin dictates the superhydrophobicity, superfluidity, superlubricity, and supersolidity at the contacting interfaces; (iv) competition between the energy density and atomic cohesive energy determines intrinsically while competition among the dislocation creation and accumulation, and heat softening determines extrinsically the superelasticity, superplasticity, superrigidity, and the extreme strength in the inverse Hall–Petch relationship of solid at the nanoscale. It is emphasized that the concepts of local binding energy density and atomic cohesive energy are more efficient than the conventional concept of free energy in describing attributes of a solid at the skin and the interface regions.

Efforts of the above have led to systematic understanding of the unusual behavior of graphene, nanostructured Silicon, ZnO, water ice, etc., and measures and techniques for practical applications.

Part IV is focused on the geometric structure, local potentials, relaxation dynamics of the hydrogen bond (O:H–O), and the associated anomalies of water and ice under cooling, compressing, and clustering. An extension of Pauling's Ice Rule results in not only the correlation between the size, separation, structure order, and mass density of molecules packing in water and ice but also the O:H–O bond as a pair of asymmetric and coupled oscillators with ultra-short-range interactions. Hydrogen proton undergoes no "frustration" in the O:H–O bond because of the asymmetric local potentials. This part verifies that: (i) Coulomb repulsion between the electron pairs on adjacent oxygen atoms and the disparity within the O:H–O bond determine the difference in nature between water and other common materials; (ii) when the environment changes, the O:H van der Waals bond and the H–O polar-covalent bond relax in the same direction but by different amounts; (iii) compression shortens and stiffens the O:H bond significantly but lengthens and softens the H–O bond via Coulomb repulsion; coordination number reduction (clusters, surface skins, and ultrathin films) causes H–O bond contraction and results in the opposite trends of O:H–O bond relaxation to that happening under compression; the bonding part with a relatively lower specific-heat contracts upon cooling, meanwhile, this part forces the other to elongate by different amounts via the repulsion. This process leads to the thermally driven density and phonon-stiffness oscillations of water and ice in four temperature regions. In the liquid and solid phases, the softer O:H bond contracts more than the stiffer H–O elongates, hence, an O:H–O cooling contraction and the seemingly regular process of cooling densification take place. In the water–ice transition phase, the H–O contracts less than the O:H elongates, leading to an O:H–O elongation and volume expansion during freezing. At temperature below 80 K, density increases slightly due to O:H–O bond angle stretching as the length and energy of the H–O and the O:H bond conserve. In ice, the O–O distance is longer than it is in water, resulting in a lower density, so that ice floats; (iv) liquid water is comprised of a high-density body of tetrahedrally coordinated structures with O:H–O bond angle and intermolecular distance fluctuations and a supersolid skin that is elastic, hydrophobic, polarized, ice-like, with two molecular layers of ultra-low density. The supersolid skin not only slipperizes ice but also enhances the surface tension of water. Modulation of the intermolecular Coulomb repulsion by replacing O with other ions results in Hofmeister series. It is emphasized that focusing on the statistical mean of all the cooperative parameters is more reliably revealing than on the instantaneous accuracy of one parameter at a time for the strongly correlated and fluctuating system of liquid water.

Apart from the perspective in each part, this work ends with a solution to the Mpemba paradox—hotter water freezes quicker than colder water does. O:H-O bond exhibits memory to emit heat at a rate depending on the initial storage. The skin supersolidity creates gradient of heat diffusion coefficient to ensure thermal current flowing outwardly. Being sensitive to the liquid volume and the drain temperature, the paradox happens only in the non-adiabatic "source-path-drain" cycling system.

It is a great pleasure to share these personal thoughts and learnings though some formulations need further refinement and improvement. Critiques from readers are cordially welcome and much appreciated.

I hope that this book will inspire fresh ways of thinking and stimulate more interest and activities toward coordination bond and electronic engineering. Directing effort to the areas of nonbonding electronics, water and soft matter electronics, quantitative phonon and electron spectroscopy, and materials gene engineering could be even more challenging, fascinating, promising, and rewarding.

I would like to express my sincere thanks to colleagues, friends, peers, and seniors for their encouragement, invaluable input, and support, to my students and collaborators for their contribution, and to my family, my wife Meng Chen and daughter Yi, for their assistance, patience, support, and understanding throughout this adventurous journey.

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